

1/PRTS

DESCRIPTION

PHOSPHORESCENT AGENT AND PRODUCTION PROCESS
THEREOF, LUMINESCENT COMPOSITION, AND ORGANIC
5 ELECTROLUMINESCENCE DEVICE AND PRODUCTION PROCESS THEREOF

TECHNICAL FIELD

The present invention relates to a phosphorescent agent
suitably usable as a material for an organic
10 electroluminescence device, and a production process
thereof, a luminescent composition containing the
phosphorescent agent, and an organic electroluminescence
device having a luminescent layer containing the
phosphorescent agent and the production process thereof.

15

BACKGROUND ART

An organic electroluminescence device is expected to be
a display device of the coming generation because it has such
excellent properties as can be formed into a thin structure,
20 driven by direct current voltage or alternating current
voltage, is wide in angle of visibility and high in visibility
because it is a self-luminescent device and fast in speed of
response, and the researches thereof are being actively
conducted.

25 As such organic electroluminescence devices, there have
heretofore been known those of a single-layer structure in
which a luminescent layer composed of an organic material is

formed between an anode and a cathode, and those of a multi-layer structures such as those of a structure having a hole-transporting layer between an anode and a luminescent layer and those of a structure having an electron-transporting layer between a cathode and a luminescent layer. These organic electroluminescence devices all emit light by recombination of electrons injected from the cathode with holes injected from the anode occurring at the luminescent layer.

As methods for forming an organic material layer in such an organic electroluminescence device, such as the luminescent layer or the hole-transporting layer, there have been known a dry method in which the organic material layer is formed by vacuum deposition of an organic material and a wet method in which a solution of an organic material dissolved therein is applied and dried to form a layer. Among these, the dry method is difficult to meet mass production because the process is complicated, and there is a limit to the formation of a layer having a large area. On the contrary, the wet method is advantageous compared with the dry method in that the process is relatively simple, and so the method can meet mass production, and an organic material layer having a large area can be formed with ease and high precision by using an ink-jet method, for example.

On the other hand, the organic material layer making up the organic electroluminescence device is required to have a high luminance. As the organic material layer, those composed of various materials have heretofore been known, and an organic

material layer containing a phosphorescent organoiridium compound or organoosmium compound as a luminous molecule has recently been proposed (Refer to pamphlet of WO 00/70655). The organic material layer is composed of a low molecular
5 organoiridium compound or organoosmium compound alone or of such a compound with a hole-transporting material such as 4,4'-N,N'-dicarbazole biphenyl or 4,4'-bis[N-(1-naphthyl)-N-phenyl-amino]biphenyl.

Further, a luminescent material composed of a
10 low-molecular iridium compound, polyvinylcarbazole and oxadiazole has been proposed in MRS 2000 Fall Meeting (November 27 to December 1, 2000, Boston, Massachusetts, USA).

However, it is difficult to obtain a luminescent layer satisfying sufficient performance in luminance when the
15 luminescent layer is formed using the above material by a wet method such as an ink-jet method.

DISCLOSURE OF THE INVENTION

The present invention has been made on the basis of the
20 foregoing circumstances and the first object thereof is to provide a phosphorescent agent with which a thin film can be formed by a wet method such as printing method or ink-jet method, and an organic electroluminescence device having high luminance can be provided.

25 The second object of the present invention is to provide a method by which the phosphorescent agent as above is produced advantageously.

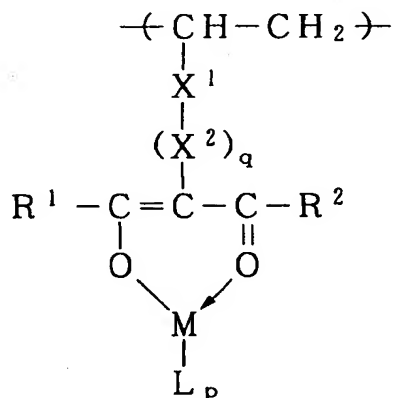
The third object of the present invention is to provide a luminescent composition by which a thin film can be formed easily and an organic electroluminescence device having high luminance can be provided.

5 The fourth object of the present invention is to provide an organic electroluminescence device having a luminescent layer that can be formed with ease by a wet method such as printing method or ink-jet method, and having high luminance.

10 The fifth object of the present invention is to provide a process for producing an organic electroluminescence device by which a luminescent layer can be formed easily by a wet method such as printing method or ink-jet method and having high luminance.

15 According to the present invention, there is provided a phosphorescent agent comprising a polymer having in its molecule a structural unit represented by the following general formula (1).

General formula (1)



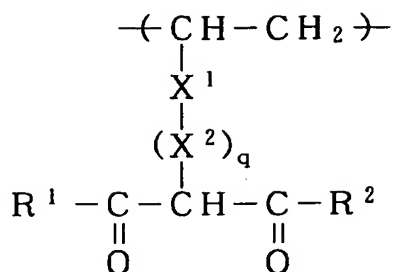
[In the general formula (1), M represents a metal atom having a valence of 2 to 4, each of R¹ and R² represents a hydrogen atom, a halogen atom or a monovalent organic group selected from an alkyl group, a cycloalkyl group, an aryl group and a heterocycle group and R¹ and R² may be either the same or different, X¹ represents a phenylene group or a oxycarbonyl group, X² represents an alkylene group, L represents an organic ligand, p is an integer of 1 to 3, and q is 0 or 1.]

The phosphorescent agent according to the present invention may preferably contain a structural unit derived from a hole-transporting monomer in the molecule of the polymer, and moreover, the polymer may preferably have a structural unit derived from an electron-transporting monomer in the molecule of the polymer.

In such a phosphorescent agent, it is preferable that the hole-transporting monomer is carbazole compound having a vinyl group, and it also is preferable that the hole-transporting monomer is carbazole compound having a vinyl group and the electron-transporting monomer is an oxadiazole compound having a vinyl group.

According to the present invention, there is provided a production process of a phosphorescent agent comprising the step of synthesizing a polymer having in its molecule the structural unit represented by the above general formula (1), by reacting a polymer having in its molecule a structural unit represented by the following general formula (2) with an organic metal complex.

General formula (2)



[In the general formula (2), each of R¹ and R² represents a
 5 hydrogen atom, a halogen atom or a monovalent organic group
 selected from an alkyl group, a cycloalkyl group, an aryl group
 and a heterocycle group, and R¹ and R² may be either the same
 or different, X¹ represents a phenylene group or a oxycarbonyl
 group, X² represents an alkylene group, and q is 0 or 1.]

10 According to the present invention, there is provided a
 luminescent composition comprising the above-mentioned
 phosphorescent agent dissolved in an organic solvent.

 According to the present invention, there is provided an
 organic electroluminescence device having a luminescent layer
 15 containing the above-mentioned phosphorescent agent.

 According to the present invention, there is provided a
 production process of the organic electroluminescence device
 comprising the steps of; applying the above-mentioned
 luminescent composition on a surface of a substrate on which
 20 a luminescent layer is to be formed, and conducting removal
 treatment for removing an organic solvent to the resultant
 coated film to form a luminescent layer.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG.1 is a cross sectional view for explanation showing a structure in an example of an organic electroluminescence device having a luminescent layer formed with a luminescent composition according to the present invention.

FIG.2 is a cross sectional view for explanation showing a structure in another example of an organic electroluminescence device having a luminescent layer formed with a luminescent composition according to the present invention.

[Description of Characters]

- 1 Transparent substrate
- 2 Anode layer
- 15 3 Hole-transporting layer
- 4 Copper-phthalocyanine layer
- 5 Luminescent layer
- 6 Electron-injecting layer
- 7 Cathode layer
- 20 8 Direct current power source

BEST MODE FOR CARRYING OUT THE INVENTION

The embodiments of the present invention will hereinafter be described in detail.

25 [Phosphorescent agent]

The phosphorescent agent according to the present invention comprises a polymer (hereinafter referred to as

"specific polymer") having in its molecule a structural unit represented by the above general formula (1). The specific polymer may be composed of a structural unit represented by the above general formula (1) only, or may also be the one having
5 an additional structural unit or units. In the case where the specific polymer has the additional structural unit, the polymer may have the structural unit represented by the above general formula (1) at a terminal or in main chain, or both at a terminal and in main chain of the molecule.

10 In the above general formula (1), M is a metal atom having a valence of 2 to 4. The metal atom thereof may preferably be a transition metal atom in group 7 through group 10 of the periodic table. Specific examples thereof include Pd, Pt, Rh, Ir, Ru, Os and Re. Among these, Ir, Os or Pt is preferable
15 because it has a large work function.

Each of R^1 and R^2 is a hydrogen atom, a halogen atom or a monovalent organic group selected from an alkyl group, an aryl group and a heterocycle group, and R^1 and R^2 may be either the same or different.

20 Specific examples of halogen atom include chlorine atom, fluorine atom and the like.

The alkyl group and the cycloalkyl group may preferably have 1 to 12 carbon atoms. Specific examples of the alkyl group include, methyl group, ethyl group, propyl group, t-butyl
25 group, hexyl group, octyl group, dodecyl group and the like, and the group may have a side chain or chains.

The aryl group and the heterocycle group may preferably

have 4 to 14 carbon atoms. Specific examples of the aryl group include phenyl group, naphthyl group, anthracenyl group, biphenyl group and the like. Specific examples of the heterocycle group include thienyl group, pyrrolyl group, furyl group, pyridyl group, pyrimidinyl group, triazinyl group, oxazolyl group, oxaziazolyl group, tetrahydrofuryl group, tetrahydrothiofuryl group and the like.

X^1 is a phenylene group or a oxycarbonyl group, X^2 is an alkylene group, and the alkylene group may preferably have 1 to 8 carbon atoms.

L is an organic ligand, and the organic ligand is formed with an organic compound having coordinating ability to the metal atom M in the general formula (1). The number p of the organic ligand is an integer of 1 to 3, and is suitably selected in accordance with the number of valence of the metal atom concerned and a stable coordination number of a neutral complex with the metal atom. More specifically, the number p of the organic ligand is selected so that the number of outer most shell electrons in the metal atom is to be 16 or 18.

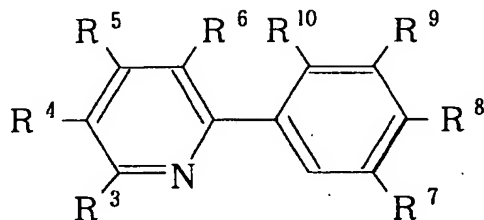
As specific examples of the organic compound forming the organic ligand include;

an organic compound forming a neutral unidentate organic ligand such as, trialkylamines, triarylamine, pyridine, quinoline, oxazole, trialkylphosphines and triarylphosphines;

an organic compound forming a unidentate organic ligand such as alkoxides such as methoxides, t-butoxides and phenoxides and carboxylates such as acetates and trifluoroacetates;

an organic compound forming a multidentate organic ligand include, acetylacetone, hexafluoroacetylacetone and β -diketones such as 5,5-dimethyl-2,4-hexadione, diamines such as ethylenediamine and dipyridyl, 9-hydroxyquinoline, picolinic acid and salicylic acid; and phenylpyridine compounds represented by the following general formula (3). These compounds may be used either alone or in combination of two or more.

10 General formula (3)



[In the general formula (3), each of R^3 through R^{10} represents a hydrogen atom, a halogen atom or a monovalent organic group independently, and among R^3 through R^{10} , a ring may be formed by adjacent two groups bonded to each other.]

Among the above-mentioned organic compounds, are preferred β -diketones and phenylpyridine compounds represented by the above general formula (3), in that chelate can be easily formed. Moreover, the phenylpyridine compound represented by the above general formula (3) is particularly preferable, since dehydrogenation of hydrogen atom at ortho-position of the 2-substituted phenyl group to pyridine ring may easily occur, and the dehydrogenated carbon atom in

the 2-substituted phenyl group may form a σ -bond with the metal atom, as well as the nitrogen atom in the pyridine ring may act as an ortho-metallation type chelating agent to coordinate with the metal atom, so that a chemically stable phosphorescent agent can be obtained and the wavelength and strength of phosphorescence by the phosphorescent agent can be controlled.

As specific examples of the phenylpyridine compound represented by the general formula (3) include,

2-phenylpyridine, 2-biphenylpyridine,

10 2-(4-(2,6-dimethylphenyl)phenyl)pyridine,

2-phenyl-4-(N,N-dimethylamino)pyridine,

2-phenyl-4-pyrrolidinopyridine,

2-phenyl-4-(N,N-diphenylamino)pyridine,

2-phenyl-4-methylpyridine,

15 2-phenyl-4,6-dimethylpyridine,

2-(2-fluorophenyl)pyridine,

2-(2,4-difluorophenyl)pyridine,

2-(2,3,4-trifluorophenyl)pyridine,

2-(2,3,4,5-tetrafluorophenyl)pyridine,

20 2-phenyl-4-methylpyridine,

2-(2-fluorophenyl)-4-methylpyridine,

2-(2,4-difluorophenyl)-4-methylpyridine,

2-(2,3,4-trifluorophenyl)-4-methylpyridine,

2-(2-naphthyl)pyridine,

25 2-phenylquinoline, 2-benzoylpyridine,

7,8-benzoquinoline, 9-anthranilpyridine,

2-(2-fluorenyl)pyridine,

2-(2-(9,10-dimethyl)fluorenyl)pyridine,
2-(2-(9,10-dihexyl)fluorenyl)pyridine,
2-(2-(9,10-dioctyl)fluorenyl)pyridine, and the like.

When the specific polymer making up the phosphorescent
5 agent of the present invention comprises the structural unit
represented by the above general formula (1) and the additional
structural unit, as the additional structural unit may
preferably be used those having a structural unit derived from
a hole-transporting monomer, or those having both of the
10 structural units derived from a hole-transporting monomer and
from an electron-transporting monomer.

As the hole-transporting monomer, may preferably be used
a carbazole derivative. As the carbazole derivative may be used
 α,β -unsaturated compound such as an alkenyl compound, a
15 (meth)acrylic compound, or a styryl compound, having a
substituted or unsubstituted carbazolyl group such as
carbazolyl group, alkylcarbazolyl group, arylcarbazolyl group
or the like. Specific examples thereof include,

N-vinylcarbazole,
20 N-(p-vinylphenyl)carbazole,
3,6-dimethyl-9-vinylcarbazole,
3,6-diethyl-9-vinylcarbazole,
3-methyl-9-vinylcarbazole,
3-ethyl-9-vinylcarbazole and the like.

25 As the electron-transporting monomer, an oxadiazole
derivative may preferably be used. As the oxadiazole derivative
may be used α,β -unsaturated compound such as an alkenyl

compound, a (meth)acrylic compound, or a styryl compound, having a substituted or unsubstituted oxadiazolyl group such as oxadiazolyl group, alkyloxadiazolyl group, aryloxadiazolyl group or the like. Specific examples thereof include,

- 2-(p-vinylphenyl)-5- β -naphthyl-1,3,4-oxadiazole,
- 2-(p-vinylphenyl)-5-biphenyl-1,3,4-oxadiazole,
- 2-phenyl-5-(p-vinylphenyl)-1,3,4-oxadiazole,
- 2- β -naphthyl-5-(4-vinylphenyl)-1,3,4-oxadiazole,
- 10 2- α -naphthyl-5-(4-vinylphenyl)-1,3,4-oxadiazole,
- 2-phenyl-5-(4-vinylphenyl)-oxadiazole,
- 2-phenyl-5-(4-vinyl-p-biphenyl)-1,3,4-oxadiazole,
- 2-(p-biphenyl)-5-(4-vinylphenyl)-1,3,4-oxadiazole,
- 2-(p-biphenyl)-5-(4-propenylphenyl)-1,3,4-oxadiazole,
- 15 2-t-butoxyphenyl-5-(4-(4-vinylphenyl)-p-biphenyl)-1,3,4-oxadiazole, or substituted compounds of these oxadiazole derivatives with an acryloyl or methacryloyl group.

A proportion of the structural unit represented by the general formula (1) in the specific polymer making up the phosphorescent agent according to the present invention, may preferably be 0.1 mol % or more, more preferably 1 mol% or more of all of structural units. If the proportion is too low, both of the luminance and the luminous efficiency tend to be low in some cases.

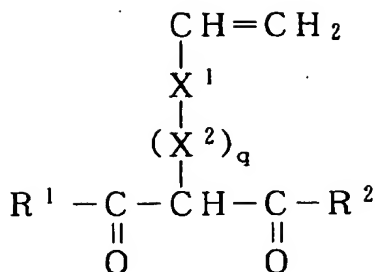
25 The specific polymer making up the phosphorescent agent of the present invention preferably has a weight average molecular weight of 500 to 1,000,000, particularly 5,000 to

500,000, in terms of polystyrene as measured by gel permeation chromatography (hereinafter referred to as "GPC"). If the weight average molecular weight is lower than 500, or higher than 1,000,000, an applicability of the after-mentioned
5 luminescent composition becomes low, hence it is not preferable.

The specific polymer making up the phosphorescent agent of the present invention can be obtained by reacting the polymer (hereinafter referred to as "specific precursor polymer")
10 having the structural unit represented by the above general formula (2) with an organic metal complex.

The specific precursor polymer can be obtained by polymerizing a monomer composition containing a compound represented by the following general formula (4),
15 specifically, a monomer composition comprising the compound represented by the following general formula (4) only, a monomer composition comprising the compound represented by the following general formula (4) and a monomer of the above-mentioned carbazole derivative, or a monomer composition
20 comprising the compound represented by the following general formula (4) and monomers of the above-mentioned carbazole derivative and the above-mentioned oxadiazole derivative.

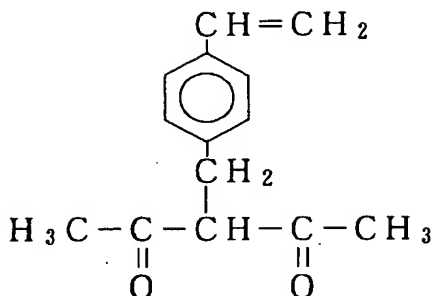
General formula (4)



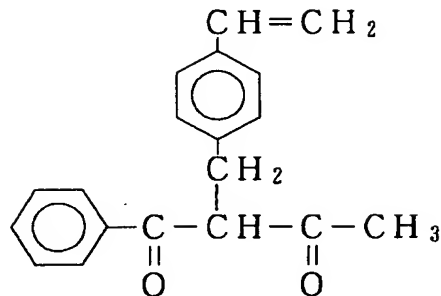
[In the general formula (4), each of R^1 and R^2 represents a hydrogen atom, a halogen atom, or a monovalent organic group selected from an alkyl group, a cycloalkyl group, an aryl group and a heterocycle group, R^1 and R^2 may be either the same or different. X^1 represents a phenylene group or a oxycarbonyl group, X^2 represents an alkylene group, and q is 0 or 1.]

As preferable specific examples of the compound represented by the general formula (4), may be mentioned such as 3-(p-vinylphenylmethylene)-pentane-2,4-dione as shown by the following formula (4-1), 3-(vinylcarbonyloxy)-pentane-2,4-dione and compounds as shown by the following formulae (4-2) to (4-4).

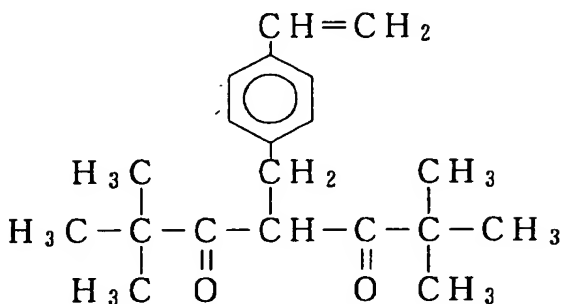
Formula (4-1)



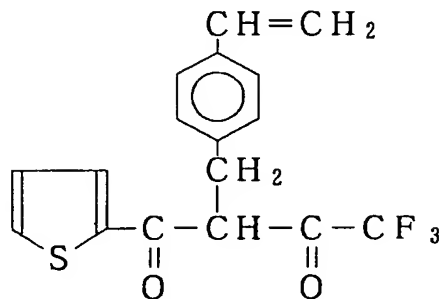
Formula (4-2)



Formula (4-3)



Formula (4-4)



As polymerizing process for polymerizing the above
 5 monomer composition may be utilized a publicly known
 polymerization processes, for example, radical polymerization
 process, cationic polymerization process, anionic
 polymerization process, or living polymerization process
 thereof.

10 When the radical polymerization process is conducted, as
 a radical polymerization catalyst, may be used a catalyst such
 as azobisisobutyronitrile, azobis-1-acetoxy-1-phenylethane
 or the like, a catalyst composed of a combination of a peroxide
 and N-oxy radical such as 4-methylsulfonyloxy-

15 2,2',6,6'-tetramethyl-1-piperidine-N-oxide, 3,3,5,5-tetra-

methyl-1-pyrroline-N-oxide or 4-oxo-2,2',6,6'-tetramethyl-1-piperidine-N-oxide, or a sulfide catalyst. A proportion of such a radical polymerization catalyst used is 0.0001 to 0.5 mol per 1 mol of the whole monomers.

5 As a solvent for polymerization, may be used amide solvents such as dimethylformamide, dimethylacetamide and N-methylpyrrolidone; hydrocarbon solvents such as benzene, toluene, xylene, hexane and cyclohexane; esters such as γ -butyrolactone and ethyl lactate; or ketone solvents such
10 as cyclohexylbenzophenone and cyclohexanone.

The reaction temperature is, for example, 60 to 200°C.

When the cationic polymerization process is conducted, as a cationic polymerization catalyst, may be used a catalyst such as HI-ZnI₂, I₂ or I₂-HI. Besides, a catalyst
15 composed of a combination of a Lewis acid and a base such as a metal halide-ether complex may also be used. A proportion of such cationic polymerization catalyst used is 0.0001 to 0.5 mol per 1 mol of the whole monomers.

As a solvent for polymerization, may be used a
20 halogenated hydrocarbon typified by methylene chloride or chlorobenzene, an ether solvent such as dibutyl ether, diphenyl ether, dioxane or tetrahydrofuran, or a high-polar solvent such as acetonitrile or nitrobenzene.

The reaction temperature is, for example, -150 to 50°C.

25 When the anionic polymerization process is conducted, as an anionic polymerization catalyst, may be used an alkali metal compound such as naphthalenepotassium or alkyllithium, an

alkaline earth metal compound such as ate-complex of barium or aluminum. A proportion of such anionic polymerization catalyst used is 0.0001 to 0.5 mol per 1 mol of the whole monomers.

As a solvent for polymerization, may be used an aromatic
 5 hydrocarbon such as toluene or benzene, an aliphatic
 hydrocarbon such as hexane or heptane, an ether compound such
 as tetrahydrofuran.

The reaction temperature is, for example, 0 to 100°C.

In the case where the specific precursor polymer
 10 comprises the structural unit represented by the above general
 formula (2) and the additional structural unit, said specific
 precursor polymer can be a random copolymer or block copolymer.
 The block copolymer can be produced by preparing a polymer
 comprising the structural unit represented by the above general
 15 formula (2) and a polymer comprising the additional structural
 unit, in advance, and then combining these polymers.

As an organic metal complex used for obtaining the
 specific polymer, is preferably used a compound represented by
 the following general formula (5).

20 General formula (5) $M_x L_y Q_z$

[In the general formula (5), M represents a metal atom having
 a valence of 2 to 4, L represents an organic ligand and Q
 represents a hydrogen atom, a halogen atom or a ligand formed
 from an alkyl group, an alkoxy group or a carboxyl compound.
 25 x is an integer of 1 to 4, y is an integer of 0 to 8, and z is
 an integer of 0 to 8 with the proviso that $y + z = 2$ to 16.]

In the general formula (5), M representing a metal atom

having a valence of 2 to 4 and L representing an organic ligand are corresponding to M and L in the above general formula (1), respectively. Specific examples of the carbonyl compounds include acetylacetone and the like.

5 In the general formula (5), Ir, Os and Pt are preferable examples for M, a phenylpyridine compound represented by the above general formula (3) is preferable example for L, and a halogen atom such as chlorine atom is preferable example for Q.

10 Specific examples of the compounds represented by the general formula (5) include,

chlorobis(2-phenylpyridine)iridium or dimer thereof,
chlorobis(2-{p-(2,6-xylyl)phenyl}pyridine)iridium or dimer thereof,

15 chlorobis(2-(2,4-difluoro)phenyl-4-methylpyridine)iridium or dimer thereof,

chlorobis(2-phenylquinoline)iridium or dimer thereof,
chlorobis(2-phenylpyridine)osmium or dimer thereof,
chlorobis(2-{p-(2,6-xylyl)phenyl}pyridine)osmium or dimer thereof,

20 chlorobis(2-(2,4-difluoro)phenyl-4-methylpyridine)osmium or dimer thereof,

chlorobis(2-phenylquinoline)osmium or dimer thereof,
chlorobis(2-phenylpyridine)platinum or dimer thereof,

25 chlorobis(2-{p-(2,6-xylyl)phenyl}pyridine)platinum or dimer thereof,

chlorobis(2-(2,4-difluoro)phenyl-4-methylpyridine)platinum

or dimmer thereof,

chlorobis(2-phenylquinoline)platinum or dimmer thereof, and the like.

Among the organic metal complexes represented by the
5 general formula (5), an organic metal complex in which M is Ir, L is an organic ligand comprised of the phenylpyridine compound represented by the above general formula (3) and Q is a chlorine atom and x is 2, y is 4 and z is 2, for example, can be obtained by reacting iridium trioxide with the
10 phenylpyridine compound represented by the above general formula (3) in a suitable reaction solvent.

As a reaction solvent, may be used a polar solvent such as glycerin, ethylene glycol derivative or propylene glycol derivative, or a mixture of the polar solvent with water.
15 Specific examples of ethylene glycol include ethylene glycol monomethylether, ethylene glycol monoethylether, ethylene glycol monobutoxyether and the like.

A proportion of the reaction solvent used is usually 100 to 10,000 weight parts per total 100 weight parts of iridium
20 trioxide and the phenylpyridine compound represented by the general formula (3).

A proportion of iridium trioxide and the phenylpyridine compound represented by the general formula (3) used may preferably be 1:2 to 1:10 in terms of molar ratio.

25 The reaction temperature is, for example, 30 to 200°C, and the reaction time is 2 to 48 hours.

The reaction of the specific precursor polymer with the

organic metal complex is preferably conducted in the suitable organic solvent under an inert gas atmosphere.

As the inert gas, may be used argon gas, nitrogen gas or the like.

5 As the organic solvent, may be used an organic compound having boiling point of 50 to 300°C under atmospheric pressure, and specific examples include tetrahydrofuran, dioxane, dimethylformamide, toluene, ethylene glycol monoethylether and the like.

10 The reaction conditions of the reaction temperature is 0 to 300°C, for example, and the reaction time is 1 to 48 hours, for example.

 A proportion of the organic metal complex used is preferably 0.1 to 100 weight parts per 100 weight parts of the precursor polymer. If the proportion of the organic metal
15 complex is too low, the reaction efficiency of the specific precursor polymer with the organic metal complex tends to become low. On the other hand, if the proportion of the organic metal complex is too high, uniformity of the respective
20 component in the reaction system tends to become low.

 A proportion of the organic solvent used is preferably 1 to 50 weight % in terms of solid concentration. If the proportion is 1 weight % or less, the reaction efficiency of the specific precursor polymer with the organic metal complex
25 tends to become low. On the other hand, if the proportion exceeds 50 weight %, solid content tends to separate out. It is hence not preferable such a lower or higher proportion.

The phosphorescent agent thus obtained emits phosphorescence having a peak wavelength within a range of 440 to 700nm for example, therefore, it is suitable for a material of the luminescent layer of the organic electroluminescence device.

According to the above phosphorescent agent, since the phosphorescent agent itself is formed by polymer, it is easily able to form a thin film by the wet method such as printing method or ink-jet method, and further, an organic electroluminescence device having high luminance can be obtained, as shown in the after-mentioned examples.

<Luminescent composition>

The luminescent composition of the present invention is formed of the above phosphorescent agent dissolved in an organic solvent.

As the organic solvent, may be used any of a various kinds of organic solvents so far as it can dissolve the phosphorescent agent used therein. Specific examples thereof include, alcohols such as butanol, octanol, ethylene glycol, propylene glycol, ethylene glycol monomethyl ether, propylene glycol monomethyl ether, ethylene glycol monoethyl ether, propylene glycol monoethyl ether, ethylene glycol monobutyl ether and propylene glycol monobutyl ether; aromatic hydrocarbons such as toluene, xylene, cyclohexylbenzene and mesitylene; esters such as ethyl acetate, butyl acetate, ethyl lactate, ethoxypropylene glycol acetate, propylene glycol monomethyl acetate and γ -butyrolactone; amides such as N-

methylypyrrolidone, formamide, dimethylformamide and dimethylacetoamide; ethers such as ethylene glycol dimethyl ether, diethylene glycol dimethyl ether, tetrahydrofuran and 1,4-dioxane; ketones such as cyclohexanone, methyl amyl ketone and methyl isobutyl ketone.

Among these, may be preferably used aromatic hydrocarbons, amides, ethers and ketones, and particularly preferred are ethyl lactate, propylene glycol monomethyl ether, propylene glycol monomethyl acetate, cyclohexanone, cyclohexylbenzene, mesitylene or the like.

A proportion of the organic solvent used is suitably selected according to the kinds of the phosphorescent agent and the like as used, however, it is generally selected within a range of 0.05 to 10 weight % in terms of solid concentration.

The luminescent composition according to the present invention may contain a polymer having a hole-transporting ability, for example, other than the above phosphorescent agent. As such polymer having the hole-transporting ability may be used a copolymer of the carbazole derivative as above-mentioned and the oxadiazole derivative as above-mentioned.

Using the luminescent composition according to the present invention, a luminescent layer of an organic electroluminescence device can be formed by steps of applying the luminescent composition on a surface of a substrate on which a luminescent layer is to be formed, and conducting removal treatment for removing the organic solvent to the resultant coated film.

As the means for applying the luminescent composition, may be used, for example, spin coating method, dipping method, roll coating method, ink-jet method, printing method or the like.

5 <Organic electroluminescence device>

FIG.1 is a cross sectional view for explanation showing a structure in an example of an organic electroluminescence device (hereinafter also referred to as "organic EL device") having a luminescent layer formed of the luminescent
10 composition according to the present invention.

According to the organic EL device, an anode layer 2 is provided on a surface of a transparent substrate 1, a hole-transporting layer 3 is provided on the anode layer 2, a luminescent layer 5 is provided on the hole-transporting layer
15 3, an electron-injecting layer 6 is provided on the luminescent layer 5, and a cathode layer 7 is provided on the electron-injecting layer 6. The anode layer 2 and the cathode layer 7 are electrically connected to a direct current power supply 8.

In the above organic EL device, as the transparent
20 substrate 1, may be used a glass substrate, a transparent resin substrate or a quartz glass substrate.

The anode layer 2 is also referred to as a hole-injecting electrode layer, and as a material making up the anode layer 2, may preferably be employed one having a high work function
25 at least 4 eV, for example. The term "work function" as used herein refers to the minimum size of work required for taking an electron out from a solid to vacuum state. As the anode layer

2, may be used, for example, an ITO (Indium Tin Oxide) film, a tin oxide (SnO_2) film, a copper oxide (CuO) film, a zinc oxide (ZnO) film and the like.

As the means for forming the anode layer 2, may be used vacuum deposition method, sputtering method or the like. A commercially available material comprises an ITO film for example is formed on a surface of a transparent substrate such as glass substrate may also be used.

The hole-transporting layer 3 is also referred to as a hole-injecting layer, and is provided for the purpose of efficiently supplying holes to the luminescent layer 5, and has a function of receiving holes from the anode layer 2 and transporting them to the luminescent layer 5.

As a material making up the hole-transporting layer 3, may preferably be employed an aromatic polymer, particularly, PEDOT [a complex of polydioxothiophene with polystyrenesulfonate (Poly(3,4)-ethylenedioxythiophene-polystyrenesulfonate), commercially available as trade name: "Baytron", (product of Bayer AG)] is preferable. As the other materials, may be employed, such as, 1,1-bis(4-di-p-aminophenyl)cyclohexane, triphenylamine derivatives and carbazole derivatives.

The hole-transporting layer 3 may be formed by a dry method such as vacuum deposition method, or by a wet method of dissolving a hole-transporting material in a proper solvent, and then applying the resultant solution by means of spin-coating method, dipping method, ink-jet method, printing

method or the like, and drying.

The thickness of the hole-transporting layer 3 is, for example, 10 to 200 nm.

The luminescent layer 5 has a function of combining
5 electrons with holes to emit the combine energy thereof as a light. The luminescent layer 5 comprises the phosphorescent agent according to the present invention.

More specifically, the luminescent layer 5 can be formed by applying the luminescent composition by means of
10 spin-coating method, dipping method, ink-jet method, printing method or the like, and drying.

The thickness of the luminescent layer 5 is, for example, 1 to 200 nm.

The electron-injecting layer 6 has a function of
15 receiving electrons from the cathode layer 7 and transporting them to the luminescent layer 5. As a material for making up the electron-injecting layer 6, may preferably be employed bathophenanthroline material (BPCs), and as the other materials may also be employed such as lithium fluoride,
20 magnesium fluoride, strontium oxide, anthraquinodimethane derivatives, diphenyl quinone derivatives, oxadiazole derivatives and perylenetetra carboxylic acid derivatives.

The electron-injecting layer 6 can be formed by a dry method such as vacuum deposition method, or by a wet method of
25 dissolving an electron-injecting material in a proper solvent, and then applying the resultant solution by means of spin-coating method, dipping method, ink-jet method, printing

method or the like, and drying.

The thickness of the electron-injecting layer 6 is, for example, 0.1 to 100 nm.

The cathode layer 7 is also referred to as an
5 electron-injecting electrode layer, and as a material making
up the cathode layer 7, may preferably be employed one having
a low work function at most 4 eV, for example. Specific examples
of the cathode layer 7 include metal films composed of
aluminum, calcium, magnesium, indium or the like, or alloy
10 films of these metals.

Such cathode layer 7 can be formed by means of vacuum
deposition method, sputtering method or the like.

In the organic EL device having the above-mentioned
structure, when direct current voltage is applied between the
15 anode layer 2 and the cathode layer 7 by the direct current power
supply 8, the luminescent layer 5 emits a light and the light
radiates through the anode layer 2 and the transparent
substrate 1.

According to the organic EL device having such a
20 structure, since the luminescent layer 5 comprises the
phosphorescent agent of the present invention, high luminance
can be obtained, and moreover, the luminescent layer 5 can
easily be formed by a wet method using the luminescent
composition of the present invention.

25 In the phosphorescent agent of the present invention
making up the luminescent layer 5, structures having
luminescent faculty are distributed or dispersed over the

luminescent agent in molecular order, and no self-vanishing by association or the like is occurred, thereby exhibiting high luminous efficiency as well as high durability.

In the organic EL device using the luminescent
5 composition according to the present invention, no limitations are to be imposed on the structure as above, and a various of changes or modifications may be incorporated.

For example, a copper-phthalocyanine layer 4 can be formed between the hole-transporting layer 3 and the
10 luminescent layer 5, as shown in the FIG.2.

The copper-phthalocyanine layer 4 lowers the energy barrier between the hole-transporting layer 3 and the luminescent layer 5, by being provided between the hole-transporting layer 3 and the luminescent layer 5, thereby,
15 injection of holes to the luminescent layer 5 can be carried out more smoothly, and energy matching can be achieved easily between the hole-transporting layer 3 and the luminescent layer 5. Further, by providing of such copper-phthalocyanine layer 4, the organic EL device having a long lifetime of use, high
20 luminous efficiency and high durability can be obtained.

Such copper-phthalocyanine layer 4 can be formed by a dry method such as vacuum deposition method or sputtering method, or by a wet method of applying a solution containing copper-phthalocyanine by means of spin-coating method,
25 dipping method, ink-jet method, printing method or the like, and drying.

The thickness of the copper-phthalocyanine layer 4

is, for example, 0.5 to 50 nm.

The present invention will hereinafter be described specifically by the following examples. However, the present invention is not limited to these examples.

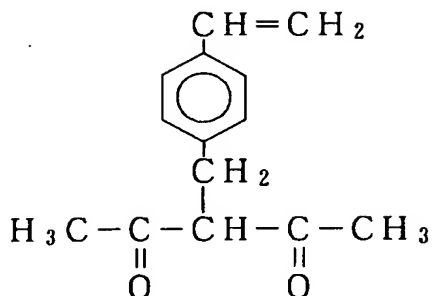
5 (1) Preparation of a specific precursor polymer:

<Preparation Example 1-1>

A nitrogen-substituted flask was charged with 1.93 g (10.0 mmol) of N-vinylcarbazole, 0.27 g (1.0 mmol) of 3-(p-vinylphenylmethylene)-pentane-2,4-dione represented by
10 the following formula (i), 0.082 g of azobisisobutyronitrile and 10 ml of dimethylformamide anhydride, and the system was heated and stirred for 30 hours at 65°C. The resultant reaction liquid was then cooled and poured into a great amount of methanol to precipitate resultant product. After the product
15 was washed and dried, thereby obtaining a white powder.

The product was a copolymer composed of 91 mol % of structural unit derived from N-vinylcarbazole and 9 mol % of structural unit derived from 3-(p-vinylphenylmethylene)-pentane-2,4-dione, and had a weight average molecular weight
20 determined by gel permeation chromatography (GPC) of 37,000 in terms of polystyrene. The copolymer is called "Precursor polymer (1)".

Formula (i)



<Preparation Example 1-2>

5 According to the same manner as in the Preparation Example 1-1 except that 0.596 g (2 mmol) of 2-(p-vinylphenyl)-5- β -naphthyl-1,3,4-oxadiazole was additionally added as a monomer, a white or slightly pale yellowish powder was obtained.

10 The product thus obtained was a copolymer composed of 77 mol % of structural unit derived from N-vinylcarbazole, 7 mol % of structural unit derived from 3-(p-vinylphenylmethyle)-pentane-2,4-dione and 16 mol % of structural unit derived from 2-(p-vinylphenyl)-5- β -naphthyl-1,3,4-oxadiazole, and had a weight average molecular weight determined by gel permeation chromatography (GPC) of 32,000 in terms of polystyrene. The copolymer is called "Precursor polymer (2)".

<Preparation Example 1-3>

20 According to the same manner as in the Preparation Example 1-1 except that 0.466 g (1.44 mmol) of 2-(p-vinylphenyl)-5-biphenyl-1,3,4-oxadiazole was additionally added as a monomer, a white or pale yellowish

powder was obtained.

The product thus obtained was a copolymer composed of 80 mol % of structural unit derived from N-vinylcarbazole, 8 mol % of structural unit derived from 3-(p-vinylphenylmethylene)-pentane-2,4-dione and 12 mol % of structural unit derived from 2-(p-vinylphenyl)-5-biphenyl-1,3,4-oxadiazole, and had a weight average molecular weight determined by the gel permeation chromatography (GPC) of 28,000 in terms of polystyrene. The copolymer is called "Precursor polymer (3)".

10 <Preparation Example 1-4>

According to the same manner as in the Preparation Example 1-1 except that 0.760 g (2 mmol) of 2-phenyl-5-(p-vinylphenyl)-1,3,4-oxadiazole was additionally added as a monomer, a white powder was obtained.

15 The product thus obtained was a copolymer composed of 78 mol % of structural unit derived from N-vinylcarbazole, 7 mol % of structural unit derived from 3-(p-vinylphenylmethylene)-pentane-2,4-dione and 15 mol % of structural unit derived from 2-phenyl-5-(p-vinylphenyl)-1,3,4-oxadiazole, and had a weight
20 average molecular weight determined by the gel permeation chromatography (GPC) of 41,000 in terms of polystyrene. The copolymer is called "Precursor polymer (4)".

<Preparation Example 1-5>

25 According to the same manner as in the Preparation Example 1-4 except that 2.8 g (10.4 mmol) of N-(p-vinylphenyl)carbazole was used instead of N-vinylcarbazole, a light beige powder was obtained.

The product thus obtained was a copolymer composed of 78 mol % of structural unit derived from N-(p-vinylphenyl) carbazole, 7 mol % of structural unit derived from 3-(p-vinylphenylmethylene)-pentane-2,4-dione and 15 mol % of structural unit derived from 2-phenyl-5-(p-vinylphenyl)-1,3,4-oxadiazole, and had a weight average molecular weight determined by the gel permeation chromatography (GPC) of 13,000 in terms of polystyrene. The copolymer is called "Precursor polymer (5)".

10 (2) Preparation of Organic metal complex:

<Preparation Example 2-1>

Mixed were 2g of iridium trichloride (III) hydrate, 5.0 g of phenylpyridine, 120 g of ethoxyethanol and 40 g of purified water, and the mixture was heated and stirred for 10 hours at 115°C under nitrogen stream. The resultant reaction liquid was cooled and deposited product was separated by filtration and then vacuum-dried, thereby obtaining 3.8 g of yellow crystal. The product was a dimer of chlorobis(2-phenylpyridine) iridium (III). The material is called "organic metal complex (1)".

20 <Preparation Example 2-2>

Mixed were 2g of iridium trichloride (III) hydrate, 3.5 g of 2-{p-(2,6-xylyl)phenyl}pyridine, 120 g of ethoxyethanol and 40g of purified water, and the mixture was heated and stirred for 24 hours at 115°C under nitrogen stream. The resultant reaction liquid was cooled and deposited product was separated by filtration and then vacuum-dried, thereby

obtaining 3.8 g of yellow crystal. The product was a dimer of chlorobis(2-{p-(2,6-xyllyl)phenyl}pyridine)iridium (III). The material is called "organic metal complex (2)".

<Preparation Example 2-3>

5 Mixed were 2g of iridium trichloride (III) hydrate, 3.0 g of 2-(2,4-difluoro)phenyl-4-methylpyridine, 120 g of ethoxyethanol and 40g of purified water, and the mixture was heated and stirred for 24 hours at 115°C under nitrogen stream. The resultant reaction liquid was cooled and deposited product
10 was separated by filtration and then vacuum-dried, thereby obtaining 4.8 g of yellow crystal. The product was a dimer of chlorobis(2-(2,4-difluoro)phenyl-4-methylpyridine)iridium (III). The material is called "organic metal complex (3)".

<Preparation Example 2-4>

15 Mixed were 2g of iridium trichloride (III) hydrate, 3.0 g of 2-phenylquinoline, 120 g of ethoxyethanol and 40g of purified water, and the mixture was heated and stirred for 18 hours at 115°C under nitrogen stream. The resultant reaction liquid was cooled and deposited product was separated by
20 filtration and then vacuum-dried, thereby obtaining 3.8 g of reddish-brown crystal. The product was a dimer of chlorobis(2-phenylquinoline)iridium (III). The material is called "organic metal complex (4)".

<Example 1>

25 A solution composed of 2.0g of the Precursor polymer (1), 0.15 g of the organic metal complex (1), 0.1 g of sodium carbonate and 50 ml of hydrous tetrahydrofuran was stirred at

room temperature for 1 hour under nitrogen stream, and then stirred for 16 hours at 80°C. Subsequently, the reaction solution was cooled and reprecipitation with methanol for purification was conducted, thereby obtaining a specific

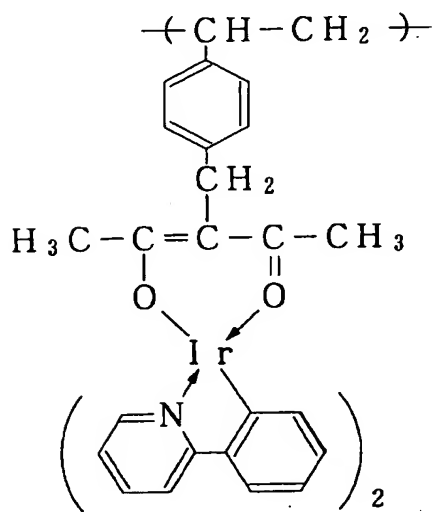
5 polymer composed of structural unit represented by the following formula (a-1) and structural unit (structural unit derived from N-vinylcarbazole) represented by the following formula (a-2). The resultant specific polymer thus obtained was dissolved in chloroform, and the solution exhibited green

10 phosphorescence spectrum. This specific polymer is called "phosphorescent agent (1)".

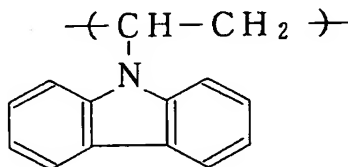
A luminescent composition was prepared by adding 5 parts by weight of the phosphorescent agent (1) to 95 parts by weight of cyclohexanone and dissolving. The composition is called

15 "luminescent composition (1)".

Formula (a-1)



Formula (a-2)



A glass substrate of 5 cm square on which an ITO film had been formed was provided, an aqueous dispersion of PEDOT (trade name: Baytron P8000, product of Bayer AG) of 2.75 % by weight was applied to the surface of the ITO film on the substrate, and the substrate thus obtained was subjected to a heat treatment at 150°C for 30 minutes, thereby forming an hole-transporting layer having a thickness of 65 nm.

The above luminescent composition (1) was then applied on the surface of the hole-transporting layer by a spin-coater and a heat treatment at 150°C for 10 minutes was conducted to form a luminescent layer having a thickness of 55 nm.

On the surface of the luminescent layer thus formed, bathophenanthroline and Cs were vacuum-deposited so as to give a molar ratio of 1:3 to form an electron-injecting layer having a thickness of 25 nm.

An aluminum film having a thickness of 100 nm was then formed in layer on the surface of the electron-injecting layer thus obtained, and then sealing with a glass material was conducted, thereby producing an organic EL device.

To the resultant organic EL device, applying 10V of direct current voltage between the ITO film for the anode layer and the aluminum film for the cathode layer to operate the organic EL device to emit light, and evaluated its emitting color and luminance. The results were that the emitting color was green and luminance was 25,000 cd/m².

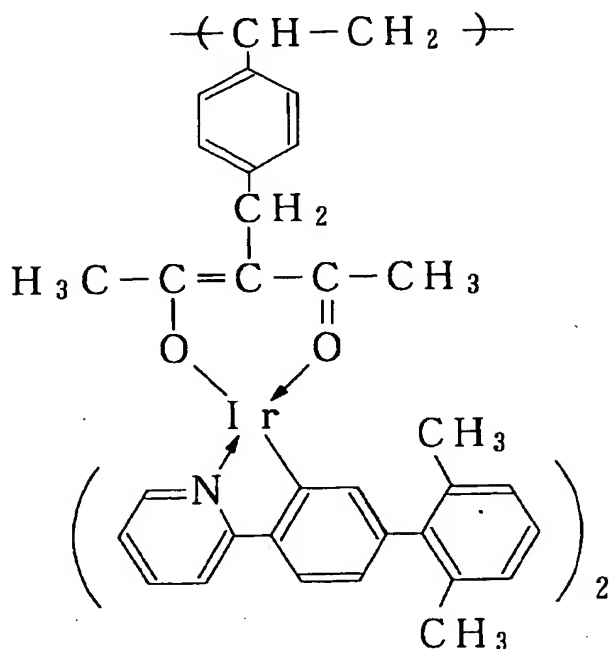
<Example 2>

A solution composed of 2.0g of the Precursor polymer

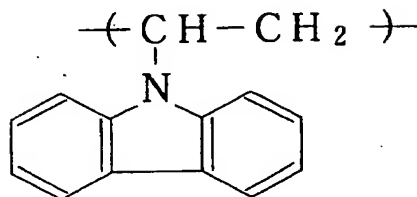
(2), 0.2 g of the organic metal complex (2), 0.1 g of sodium carbonate and 50 ml of hydrous tetrahydrofuran was stirred at room temperature for 1 hour under nitrogen stream, and then stirred for 18 hours at 50°C. Subsequently, the reaction solution was cooled and reprecipitation with methanol for purification was conducted, thereby obtaining a specific polymer composed of structural unit represented by the following formula (b-1), structural unit (structural unit derived from N-vinylcarbazole) represented by the following formula (b-2) and structural unit (structural unit derived from 2-(p-vinylphenyl)-5- β -naphthyl-1,3,4-oxdiazole) represented by the following formula (b-3). The resultant specific polymer thus obtained was dissolved in chloroform, and the solution exhibited green phosphorescence spectrum. This specific polymer is called "phosphorescent agent (2)".

A luminescent composition was prepared by adding 5 parts by weight of the phosphorescent agent (2) to 95 parts by weight of cyclohexanone and dissolving. The composition is called "luminescent composition (2)".

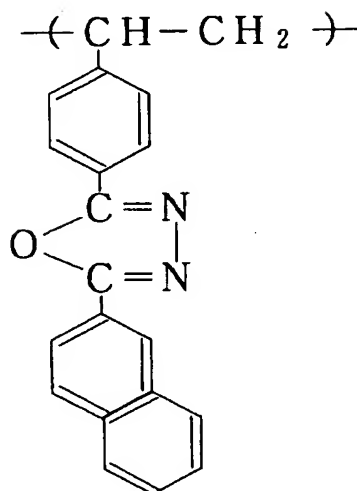
Formula (b-1)



Formula (b-2)



Formula (b-3)



An organic EL device was produced in the same manner as Example 1 except that the luminescent composition (2) was used instead of the luminescent composition (1), and evaluated its emitting color and luminance. The results were that the emitting color was green and luminance was 35,000 cd/m².

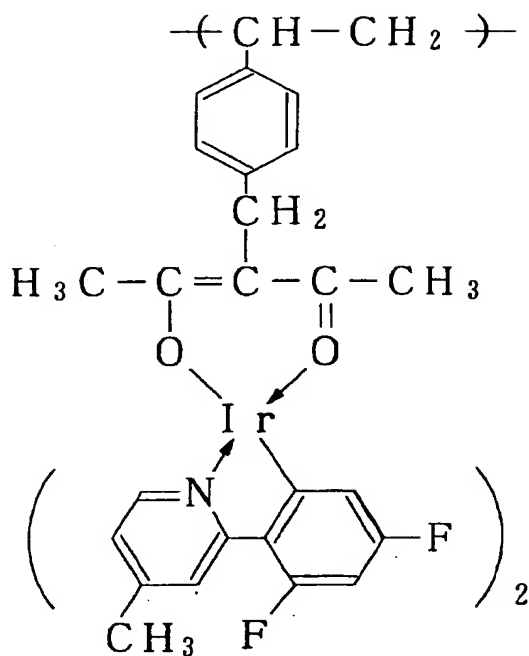
<Example 3>

A solution composed of 2.0g of the Precursor polymer (3), 0.18 g of the organic metal complex (3), 0.1 g of sodium carbonate and 50 ml of hydrous tetrahydrofuran was subjected to reaction for 48 hours at 50°C under nitrogen stream. Subsequently, the reaction solution was cooled and

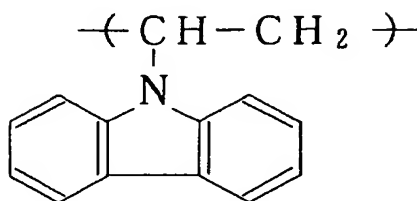
reprecipitation with methanol for purification was conducted, thereby obtaining a specific polymer composed of structural unit represented by the following formula (c-1), structural unit (structural unit derived from N-vinylcarbazole) represented by the following formula (c-2) and structural unit (structural unit derived from 2-(p-vinylphenyl)-5-biphenyl-1,3,4-oxdiazole) represented by the following formula (c-3). The resultant specific polymer thus obtained was dissolved in chloroform, and the solution exhibited bluish green phosphorescence spectrum. This specific polymer is called "phosphorescent agent (3)".

A luminescent composition was prepared by adding 5 parts by weight of the phosphorescent agent (3) to 95 parts by weight of cyclohexanone and dissolving. The composition is called "luminescent composition (3)".

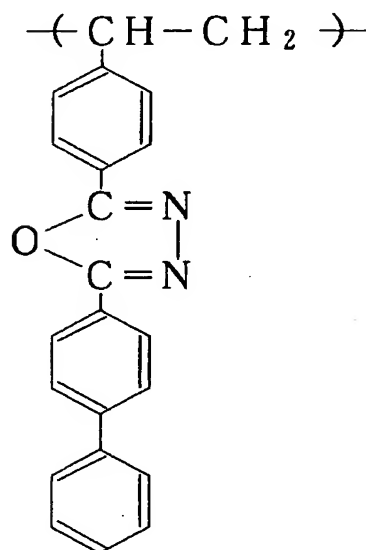
Formula (c-1)



Formula (c-2)



Formula (c-3)



An organic EL device was produced in the same manner as
 5 Example 1 except that the luminescent composition (3) was used
 instead of the luminescent composition (1), and evaluated its
 emitting color and luminance. The results were that the
 emitting color was blue and luminance was 2,000 cd/m².

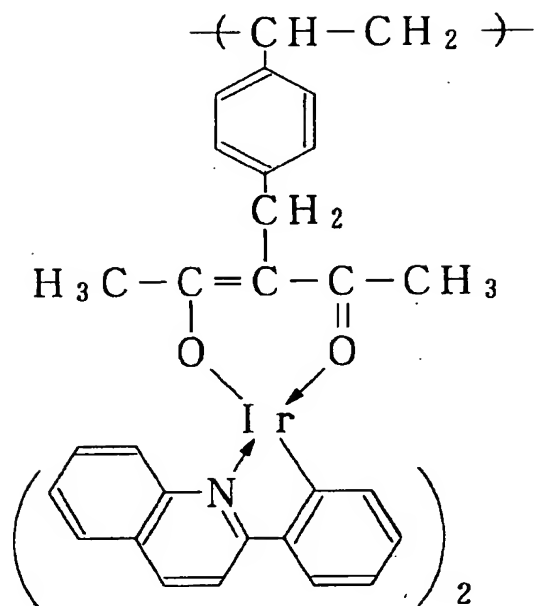
<Example 4>

10 A solution composed of 2.0g of the Precursor polymer
 (4), 0.18 g of the organic metal complex (4), 0.1 g of sodium
 carbonate and 50 ml of hydrous tetrahydrofuran was stirred for

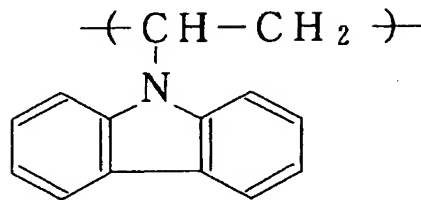
6 hours at 80°C under nitrogen stream. Subsequently, the reaction solution was cooled and reprecipitation with methanol for purification was conducted, thereby obtaining a specific polymer composed of structural unit represented by the following formula (d-1), structural unit (structural unit derived from N-vinylcarbazole) represented by the following formula (d-2) and structural unit (structural unit derived from 2-phenyl-5-(p-vinylphenyl)-1,3,4-oxdiazole) represented by the following formula (d-3). The resultant specific polymer thus obtained was dissolved in chloroform, and the solution exhibited red phosphorescence spectrum. This specific polymer is called "phosphorescent agent (4)".

A luminescent composition was prepared by adding 5 parts by weight of the phosphorescent agent (4) to 95 parts by weight of cyclohexanone and dissolving. The composition is called "luminescent composition (4)".

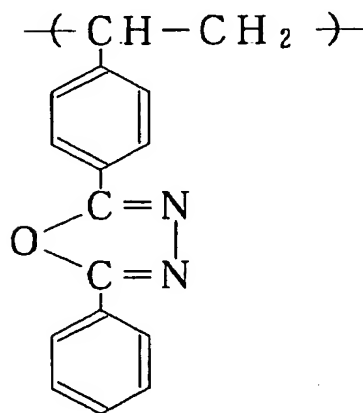
Formula (d-1)



Formula (d-2)



Formula (d-3)



An organic EL device was produced in the same manner as
 5 Example 1 except that the luminescent composition (4) was used
 instead of the luminescent composition (1), and evaluated its
 emitting color and luminance. The results were that the
 emitting color was red and luminance was 13,000 cd/m².

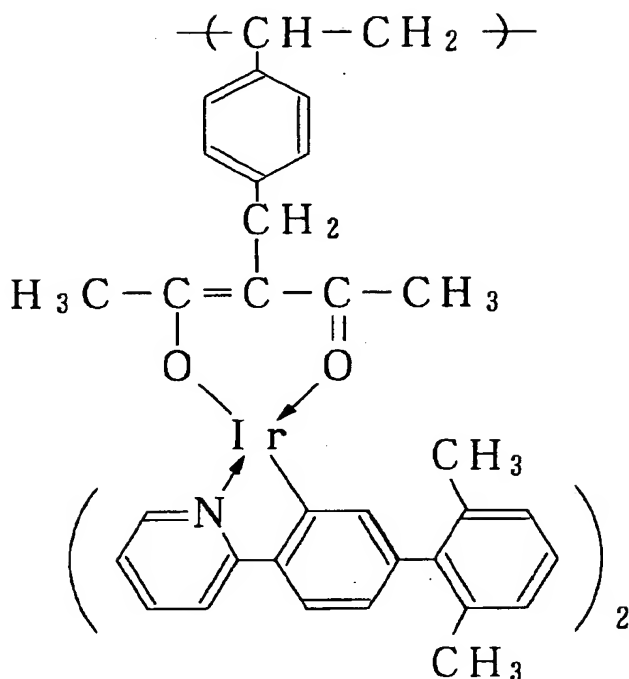
<Example 5>

10 The processes were conducted as in the same manner as
 Example 2 except that the Precursor polymer (5) was used instead
 of the Precursor polymer (2), thereby obtaining a specific
 polymer composed of structural unit represented by the
 following formula (e-1), structural unit (structural unit

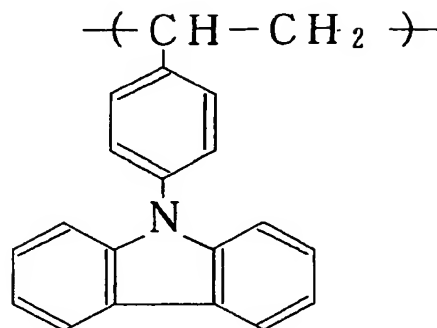
derived from N-(p-vinylphenyl)carbazole) represented by the following formula (e-2) and structural unit (structural unit derived from 2-phenyl-5-(p-vinylphenyl)-1,3,4-oxdiazole) represented by the following formula (e-3). The resultant
5 specific polymer thus obtained was dissolved in chloroform, and the solution exhibited green phosphorescence spectrum. This specific polymer is called "phosphorescent agent (5)".

A luminescent composition was prepared by adding 5 parts by weight of the phosphorescent agent (5) to 95 parts by weight
10 of cyclohexanone and dissolving. The composition is called "luminescent composition (5)".

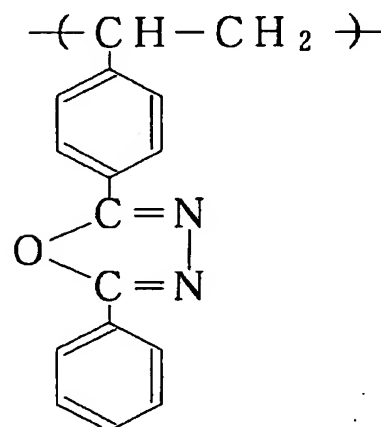
Formula (e-1)



Formula (e-2)



Formula (e-3)



An organic EL device was produced in the same manner as Example 1 except that the luminescent composition (5) was used instead of the luminescent composition (1), and evaluated its emitting color and luminance. The results were that the emitting color was green and luminance was 12,000 cd/m².
 <Comparative Example 1>

A comparative luminescent composition was prepared by dissolving 2 g of the Precursor polymer (1) and 0.15 g of the organic metal complex (1) in 40 g of cyclohexanone.

An organic EL device was produced in the same manner as

Example 1 except that the comparative luminescent composition was used instead of the luminescent composition (1), and evaluated its emitting color and luminance. The results were that the emitting color was blue and luminance was 50 cd/m².

5

EFFECT OF THE INVENTION

According to the phosphorescent agent of the present invention, a thin film thereof can be formed easily by a wet method such as printing method or ink-jet method, and there can be provided an organic electroluminescence device having high luminance.

According to the production process of the phosphorescent agent of the present invention, the above phosphorescent agent can be produced advantageously.

15 According to the luminescent composition of the present invention, a thin film can be formed easily, and there can be provided an electroluminescence device having high luminance.

The organic electroluminescence device according to the present invention has a luminescent layer which can be easily formed by a wet method such as printing method or ink-jet method, and performs high luminance.

20 According to the production process of the organic electroluminescence device of the present invention, a luminescent layer can be formed easily by a wet method such as printing method or ink-jet method, there can be produced an organic electroluminescence device performing high luminance.

25